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Thermochimica Acta 441 (2006) 137–143

thermochimica acta

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Phase behavior and a modified Kwei equation for ternary polymer blends containing stereoregular PMMA

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Received 8 August 2005; received in revised form 2 December 2005; accepted 11 December 2005

Abstract

Previously, poly(methyl methacrylate) (PMMA) was found to be almost immiscible with poly(vinyl acetate) (PVAc) regardless of tacticity of PMMA and casting solvent. Poly(vinyl phenol) (PVPh) was found successful previously in making immiscible atactic PMMA/PVAc miscible. In this investigation, tacticity effect of PMMA on a ternary composed of PMMA, PVAc and PVPh was studied. Isotactic PMMA ternary was shown to be miscible in all the studied compositions on the basis of single T_g observation. However, syndiotactic PMMA ternary demonstrated immiscibility at ca. 25% PVPh and miscibility was observed at higher PVPh concentrations. A modified Kwei equation based on the binary interaction parameters was proposed to describe the experimental T_g of the miscible ternary almost quantitatively.

Keywords: Ternary blends; PMMA; Stereoregular; Kwei equation

1. Introduction

Ternary blends are gaining importance in the field of polymers through years. The first systematic study on ternary blends was reported by Kwei et al. [1]. In their study, the addition of poly(vinylidene fluoride) (PVDF) to the immiscible pair poly(methyl methacrylate) (PMMA)/poly(ethyl methacrylate) (PEMA) was studied and found to be miscible. A list of ternaries investigated has been considerably enlarged since then [2–8]. In nearly all these blends, a third component either a homopolymer or copolymer is added to make an immiscible pair homogeneous. Miscibility is often achieved in cases where this third component is miscible with other polymers.

Zhang et al. [9] have reported an interesting review on the effect of hydrogen bonding on the phase behavior of ternary polymer blends. If the ternary polymer blends are represented by polymers 1–3, polymer 1 is the co-solvent. The ΔK effect (by analogy to the common known $\Delta\chi$ effect) proposed by them reflects the difference in the 'chemical' interaction between the self-association polymer and the other polymers in the mixture (i.e. the difference between 1–2 and 1–3 interactions). If the intermolecular interaction of 1–2 pair is stronger than the 1–3 pair, the ΔK effect is assumed to be strong. The $\Delta\chi$ effect indicates the difference in the physical interaction (often represented by difference in solubility parameter) between two pairs similar to the ΔK effect. Zhang et al. [9] concluded from their simulations that:

1. It will be difficult to find ternary polymer blends that exist in a single phase over a wide composition range. Only in very rare cases, where the 'physical' ($\Delta\chi$) and 'chemical' (ΔK) interaction differences are negligible or finely balanced, can we expect to find miscible ternary polymer blends.
2. In most cases, an immiscible binary blend cannot be made homogeneous by introducing a small amount of a third polymer (compatibilizer).
3. While the presence of specific intermolecular interaction enhances the probability of forming a homogeneous ternary polymer blend, they can concurrently exacerbate the situation through the ΔK effect, which promotes phase separation.

Through the years, especially studies of stereoregular PMMA with other polymers were published in our laboratory. In a previous study [10], isotactic PMMA and atactic PMMA were found to be miscible with poly(vinyl phenol) (PVPh) on the basis of calorimetry data when cast from 2-butanone. However, syn-

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doi:10.1016/j.tca.2005.12.013

diotactic PMMA formed partially miscible blends with PVPh. The miscibility of PMMA/PVAc blends has been controversial through the years. Through careful sample preparations and examinations, in another previous study of ours [11] PMMA and poly(vinyl acetate) (PVAc) were determined to be almost completely immiscible regardless of tacticity of PMMA and casting solvent. The results are in agreement with recent literature. The pursuit of miscible ternary blends in this lab led us to one of our recent results [12]. The results demonstrated that addition of PVPh into immiscible atactic PMMA/PVAc was proven to be successful in making them miscible. The miscibility of the ternary was probably driven by weak $\Delta\chi$ and ΔK effects in concert. The weak $\Delta\chi$ effect is because PVAc has a similar structure to PMMA. A slight difference between the aPMMA/PVPh interaction and the PVAc/PVPh interaction causes the ΔK effect to be insignificant.

Motivated by previous success, now we turn our attention to tacticity effect of PMMA in the same blends. A ternary blend consisting of isotactic (or syndiotactic) PMMA, PVAc and PVPh was prepared and investigated calorimetrically. FTIR was used to characterize the existing hydrogen bonding between PVAc (or PMMA) and PVPh. The role of PVPh as co-solvent and the effect of tacticity of PMMA on the miscibility of the ternary blends were evaluated and reported. A modified Kwei equation for ternary polymer blends based on the binary interaction parameters was proposed probably for the first time and presented in this article to describe the glass transition temperatures of the miscible ternary quite satisfactorily.

2. Experimental

2.1. Materials

Isotactic and syndiotactic PMMA (designated as iPMMA and sPMMA), PVAc and PVPh were all purchased from Polysciences, Inc., Warrington, PA. According to manufacturer information, the molecular weights (M_ws) of iPMMA (or sPMMA) and PVAc were 100,000 and 160,000 g/mol, respectively. The M_w value for PVPh was 9000–11000 g/mol.

2.2. Film preparation

Thin films of the following binary and ternary polymer blends in different weight fractions were made by solution casting from 2-butanone onto glass plates. The actual weight compositions of the binary and ternary blends are shown later in Tables 1–4. 2-Butanone is American Chemical Society (A.C.S.) reagent purchased from Aldrich Chemical Company, Inc., Milwaukee, WI. The final drying step for all the films took place in a vacuum oven at 130 °C for about 16–24 h. Then the films were cooled to room temperature slowly by air to make as-cast samples. The as-cast samples were later used for DSC studies.

2.3. Differential scanning calorimetry (DSC)

Glass transition temperatures (T_gs) of the polymer blends were determined by a DuPont DSC Q1000 thermal analyzer. The scanning range for temperature was from −10 to 210 °C and a heating rate of 20 °C/min was used in every measurement. The experiments were often performed in two consecutive scans in the ambient environment of nitrogen gas at a flow rate of 40 ml/min. In the first thermal scan, the samples stayed at 210 °C for 2 min. Then the samples were cooled to −10 °C using a cool-

Table 1
Glass transition temperatures of PVAc/PMMA blends

	T_g (°C)	ΔT_g (°C)
PVAc/sPMMA		
1. (0/100)	117.8	18
2. (25.0/75.0)	37.3, 122.6	8, 10
3. (50.0/50.0)	43.1, 122.7	7, 10
4. (74.9/25.1)	39.5, 120.8	6, 11
5. (100/0)	45.9	7
PVAc/iPMMA		
1. (0/100)	73.3	14
2. (25.0/75.0)	44.3, 71.7	6, 11
3. (50.0/50.0)	39.1, 68.5	7, 18
4. (74.9/25.1)	39.5, 69.5	6, 11
5. (100/0)	45.9	7

Table 2
Glass transition temperatures of PVAc/PVPh blends

PVAc/PVPh	T_g (°C)	ΔT_g (°C)	T_{gF} (°C)
1. (0/100)	116.3	19	–
2. (25.0/75.0)	115.1	11	95.9
3. (50.0/50.0)	87.9	11	77.6
4. (75.0/25.0)	56.9	11	61.0
5. (100/0)	45.9	7	–

Table 3
Glass transition temperatures of PVPh/sPMMA/PVAc blends

PVPh/sPMMA/PVAc	T_g (°C)	ΔT_g (°C)
1. (25.0/18.8/56.2)	62.4, 125.8	13, 13
2. (50.0/12.5/37.5)	93.3	16
3. (75.0/6.3/18.7)	105.8	17
4. (25.0/37.5/37.5)	67.1, 123.3	13, 9
5. (49.9/25.0/25.1)	102.2	28
6. (74.9/12.6/12.5)	114.1	17
7. (25.1/56.2/18.7)	76.5, 121.2	11, 14
8. (49.9/37.6/12.5)	118.8	26
9. (75.0/18.7/6.3)	133.7	18

Table 4
Glass transition temperatures of PVPh/iPMMA/PVAc blends

PVPh/iPMMA/PVAc	T_g (°C)	ΔT_g (°C)
1. (25.0/18.8/56.2)	60.2	13
2. (50.0/12.5/37.5)	90.5	14
3. (75.0/6.3/18.7)	99.6	16
4. (25.0/37.5/37.5)	66.2	20
5. (49.8/25.1/25.1)	102.9	18
6. (75.0/12.5/12.5)	123.5	16
7. (25.0/56.2/18.8)	81.6	24
8. (50.1/37.4/12.5)	107.0	25
9. (75.0/18.7/6.3)	129.9	16

ing rate of 20 °C/min. The inflection point of the specific heat jump of a second thermal scan was taken as the glass transition temperature. The cooling rate was proven to be fast enough to produce virtually the same results as quenching. ΔT_g is calculated as the difference between the onset and end points of the glass transition temperature region. The error of T_g determination is estimated to be ca. ±2 °C.

2.4. Fourier transform infrared spectroscopy (FTIR)

Most of the binary polymers were ground with KBr powder to make samples for FTIR studies. For some binary polymers (not brittle ones), the polymers were cast directly onto KBr windows. Samples for ternary polymers with PMMA/PVAc wt ratio 1/1 and various PVPh compositions were also cast onto KBr windows. All the aforementioned samples were subjected to thermal treatments similar to those for the DSC samples. Spectra were obtained with a Perkin-Elmer FTIR 2000 spectrometer at room temperature. Sixty-four scans at a resolution of 4 cm^{-1} was signal averaged. The wave-number range was 400–4000 cm^{-1}.

3. Results and discussion

Thermal scans of calorimetry were not shown for brevity. The calculated glass transition temperature data are presented in the following section.

3.1. PMMA/PVAc blends

Table 1 presents the glass transition temperatures (T_gs) of PMMA/PVAc blends. It is obvious that PMMA and PVAc are not miscible regardless of tacticity because of the observation of two T_gs. The low T_g of PVAc compared to pure PVAc is mainly due to the error of T_g determination. ΔT_g values of the PMMA/PVAc blends are also listed in Table 1 for reference. Taking into account the error of T_g determination, the blends phase separated into highly pure PMMA and PVAc phases. Previous study [11] shows that casting solvent and tacticity of PMMA have little effect on the miscibility of PMMA with PVAc. Through the calculation of phase compositions of two immiscible phases, the blends prepared from tetrahydrofuran (THF) show a little more partial miscibility than the ones cast from chloroform. Among the three tactic PMMAs, iPMMA was found previously [11] to show the highest mutual solubility with PVAc when the blends were cast from THF. The slight T_g depression observed in iPMMA blends in this study also showed that solubility of PVAc in iPMMA is a little better than sPMMA.

3.2. Binary blends with PVPh

Table 2 presents the glass transition temperatures of PVAc/PVPh blends. Single composition dependent T_g was detected in the blends indicating miscibility. The T_g of PVPh was low compared to previous studies [12] likely because of low molecular weight and sample preparation difference. The T_{gF} values tabulated in Table 2 represent the Fox prediction. The Fox equation [13] is shown below as in Eq. (1):

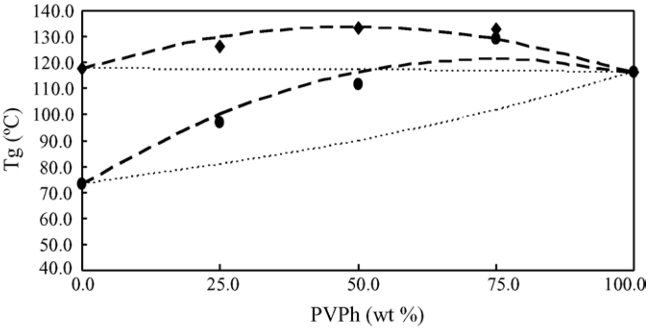

Fig. 1. Glass transition temperatures of miscible PMMA/PVPh polymer blends: (♦) sPMMA; (●) iPMMA; (- - -) the simplified Kwei equation; (· · ·) the Fox eq.

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad (1)$$

where T_g is the glass transition temperature of a blend, T_{gi} and w_i are the glass transition temperature and the weight fraction of polymers i, respectively ($i = 1, 2$). A comparison between experimental T_g and Fox estimation shows that experimental T_g value is larger than or approximately equal to T_{gF} in agreement with previous result [10]. The use of the Kwei equation for fitting T_g of PVAc/PVPh blends is shown later in Section 3.3.

The glass transition temperatures of PMMA/PVPh blends are illustrated in Fig. 1. For iPMMA/PVPh and sPMMA/PVPh blends, miscibility was detected on the basis of single T_g observation. A positive T_g deviation from weight average is likely due to hydrogen bonding existing between PMMA and PVPh. Previously [11], when PVPh of $M_w = 300{,}000$ g/mol was blended with sPMMA the blends were found to be partially miscible. However in the same study, iPMMA was miscible with PVPh but the blends T_g did not show a parabolic dependence. Interestingly in this investigation, iPMMA and sPMMA were found both miscible with a low molecular weight PVPh. Their T_g values demonstrated approximately a parabolic dependence.

Several empirical equations in literature have been proposed to describe the composition dependence of T_g of miscible blends that involve strong specific interactions. Since there are not many data points, the following equation is chosen to describe the experimental data. The simplified Kwei equation [14]:

$$T_g = w_1 T_{g1} + w_2 T_{g2} + q w_1 w_2 \qquad (2)$$

where all the symbols except q have the same definitions as in Eq. (1). And q is a parameter that depends on the net polymer–polymer interaction. q values were calculated at three compositions individually by using blend T_g and component T_g. An average of q values was taken. q values of 66.8 and 86.2 were obtained to describe the parabolic T_g dependence of the sPMMA/PVPh and iPMMA/PVPh blends approximately well, respectively. The correlation coefficient between prediction and data is not high likely because of few data points. Judging from the magnitude of q, iPMMA forms stronger hydrogen bonds with PVPh than sPMMA in agreement with previous findings [10].

FTIR spectra of all the prepared binary blends were performed but not reported here. The results are in agreement with previous findings [10–12]. Evidence of hydrogen bonds formed between carbonyl polymer (PVAc, PMMA) and phenol polymer (PVPh) was detected. Through careful IR investigation, Zhang et al. [9] reported the inter-association constant between PVAc and PVPh is slightly larger than that between aPMMA and PVPh. In reference [10], iPMMA and aPMMA were found to be miscible with PVPh. However, sPMMA formed partially miscible blends with PVPh. Also in this study, q value of iPMMA/PVPh blends obtained from the Kwei equation is larger than that of sPMMA/PVPh blends indicating stronger inter-hydrogen bonding. Therefore the probable inter-hydrogen bonding order in the related binary blends is as the following:

PVAc–PVPh $\geqq$ iPMMA–PVPh $\approx$ aPMMA–PVPh $>$ sPMMA–PVPh

3.3. Ternary blends

The FTIR spectra of one PVPh/PMMA/PVAc (ca. 25.0/37.5/37.5) ternary blend are used (not shown) as a demonstration of tacticity effect on the degree of hydrogen bonding. The spectra did not exhibit marked difference in hydroxyl and carbonyl absorption when either iPMMA or sPMMA was present in the blends. However, the calorimetry data in the following paragraph showed different phase behaviors observed in the iPMMA ternary and the sPMMA ternary.

The glass transition temperatures of the PMMA/PVAc/PVPh blends are tabulated in Tables 3 and 4 in the order of sPMMA and iPMMA, respectively. For sPMMA ternaries, the blends showed a single T_g except for the ones with ca. 25% PVPh. The 25% PVPh ternaries exhibited two T_g values indicating immiscibility. However, for all nine studied blend compositions in the iPMMA ternaries (shown in Table 4), they all demonstrated single T_g indicating miscibility. ΔT_g values of the aforementioned blends are also tabulated in Tables 3 and 4 for reference. There is a slightly ΔT_g broadening phenomenon observed in the miscible sPMMA and iPMMA ternaries and this occurs quite often in multi-component system. Why does the iPMMA ternary show better miscibility than the sPMMA ternary? The results may be interpreted as follows. Solubility between iPMMA and PVAc better than that between sPMMA and PVAc causes the $\Delta\chi$ effect to be smaller. The interaction between PVAc and PVPh is close in magnitude to that between iPMMA and PVPh. However, the difference in PVAc/PVPh and sPMMA/PVPh interactions is likely larger. Therefore the sPMMA ternaries probably demonstrated slightly stronger ΔK effect than iPMMA ternaries. In summary, small $\Delta\chi$ effect and weak ΔK effect causes the iPMMA ternaries to be more miscible than sPMMA ternaries.

In comparison with PEMA/PMMA/PVPh blends [15], the PVAc/sPMMA(or iPMMA)/PVPh blends demonstrated better miscibility behaviors. Adding of 60% of PVPh was needed to make immiscible PEMA/PMMA pairs homogeneous.

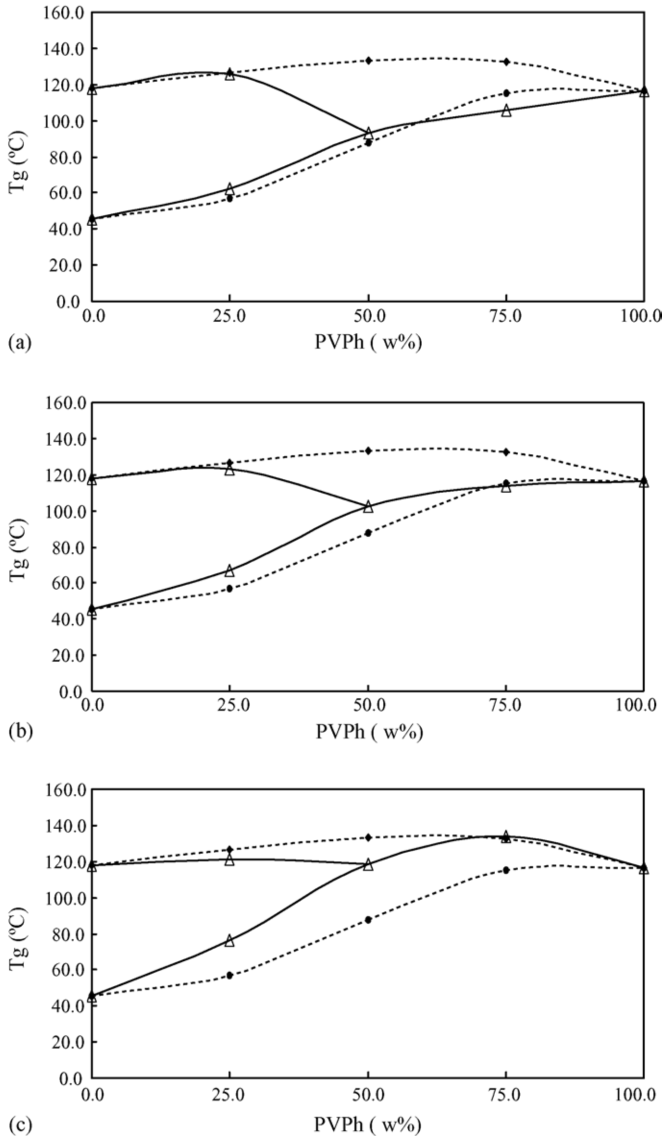

Fig. 2. (a) Change of T_g of the ternary blends with PVPh composition (sPMMA/PVAc wt ratio = 1/3): (△) data point; (♦) sPMMA/PVPh blends; (●) PVAc/PVPh blends (curves drawn for viewing). (b) Change of T_g of the ternary blends with PVPh composition (sPMMA/PVAc wt ratio = 1/1): (△) data point; (♦) sPMMA/PVPh blends; (●) PVAc/PVPh blends (curves drawn for viewing). (c) Change of T_g of the ternary blends with PVPh composition (sPMMA/PVAc wt ratio = 3/1): (△) data point; (♦) sPMMA/PVPh blends; (●) PVAc/PVPh blends (curves drawn for viewing).

However, addition of 25–50% of PVPh was sufficient to make PVAc/PMMA blends miscible. The reason is likely PVAc and PMMA exhibit partial miscibility and PEMA and PMMA are immiscible. The other possible cause is the difference between PEMA/PVPh and PMMA/PVPh interactions is large. Therefore the PEMA/PMMA/PVPh blends probably exhibit stronger ΔK effect than PVAc/PMMA/PVPh blends.

For the purpose of illustrating co-solvent effect of PVPh, the T_g values of the ternaries with PMMA/PVAc wt ratios of (1/3, 1/1 and 3/1) were plotted in Fig. 2(a–c) and Fig. 3(a–c) in the order of sPMMA and iPMMA, respectively. Results of the corresponding binaries (PMMA/PVPh and PVAc/PVPh blends) were also included in Figs. 2 and 3 for comparison. Note the drawn dashed curves in Fig. 2(a–c) and Fig. 3(a–c) are for viewing only and do not represent fits to any equation. The single T_g criterion for mis-

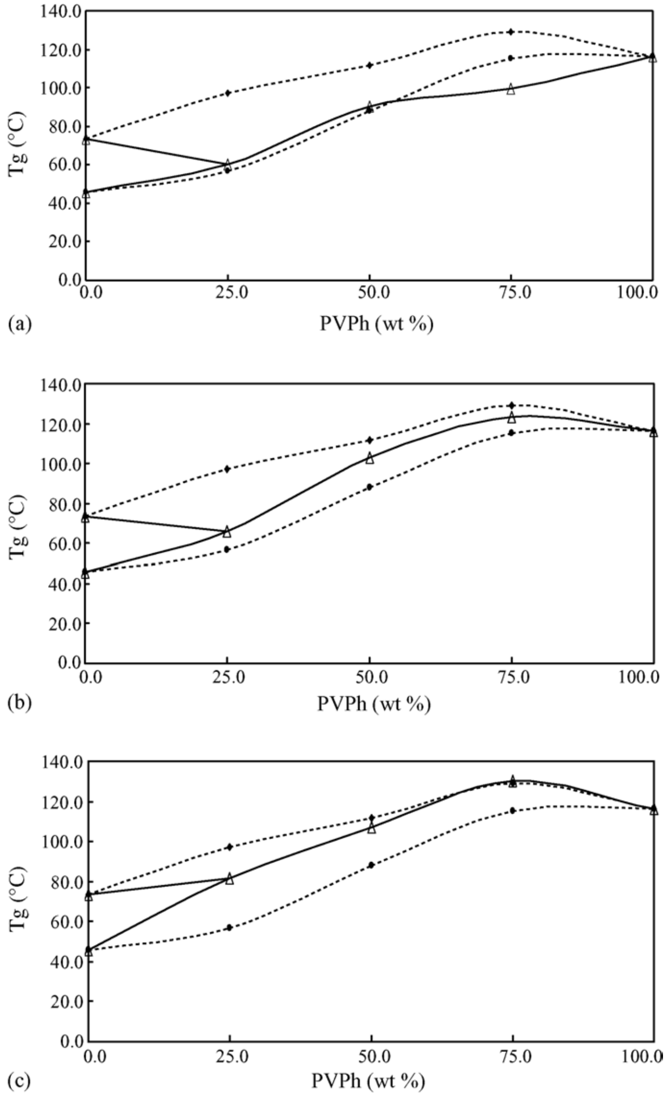

Fig. 3. (a) Change of T_g of the ternary blends with PVPh composition (iPMMA/PVAc wt ratio = 1/3): (△) data point; (♦) iPMMA/PVPh blends; (●) PVAc/PVPh blends (curves drawn for viewing). (b) Change of T_g of the ternary blends with PVPh composition (iPMMA/PVAc wt ratio = 1/1): (△) data point; (♦) iPMMA/PVPh blends; (●) PVAc/PVPh blends (curves drawn for viewing). (c) Change of T_g of the ternary blends with PVPh composition (iPMMA/PVAc wt ratio = 3/1): (△) data point; (♦) iPMMA/PVPh blends; (●) PVAc/PVPh blends (curves drawn for viewing).

cibility is used in our ternary system. The ternary T_g values of the blends with sPMMA/PVAc wt ratios ca. 1/3 and 1/1 (as shown in Fig. 2(a–b)) showed similar behavior. Immiscible ternary's two T_g values are close to T_g of corresponding binaries. For miscible ternary, the T_g values are close to or sometimes smaller than low T_g of corresponding binaries. However, the situation for the ternary with sPMMA/PVAc wt ratio ca. 3/1 is quite different. First, the immiscible ternary's two T_gs are close to each other although still located in between corresponding binaries with the same PVPh composition. Secondly, the T_g values of miscible ternary are close to or even equal to high T_g of corresponding binary. It can be deduced that the ternary might probably be miscible with the sPMMA/PVAc wt ratio higher than 3/1 even at 25% PVPh concentration. Although the iPMMA ternaries showed miscible behavior in the nine studied compositions, the relationship between their T_g values and two corresponding binaries is quite different in various iPMMA/PVAc wt ratios. Fig. 3(a) illustrates that the iPMMA/PVAc(1/3) ternary T_g are close to or smaller than the low T_g of corresponding binaries. For the ternaries with iPMMA/PVAc(1/1) in Fig. 3(b), the T_g values are located in the middle of two corresponding binaries. With increasing PVPh composition in the ternaries, the T_g values of iPMMA/PVAc(3/1) ternaries are approaching the high T_g of corresponding binary.

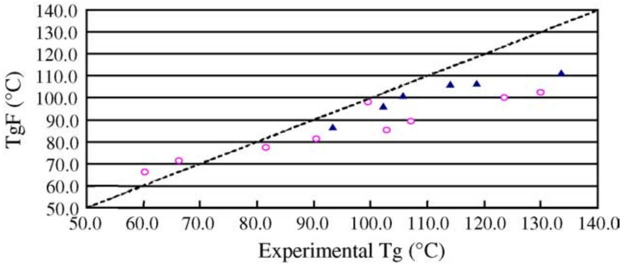

Fig. 4. Fox predicted T_g vs. experimental T_g: (▲) sPMMA; (○) iPMMA.

For polymer blends with weak or no interaction, the Fox equation seems to predict the glass transition temperature quite well. The T_g values of the ternary blends(designated as T_{gF}) were estimated using PMMA, PVAc and PVPh's T_gs in an extended Fox equation:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} + \frac{w_3}{T_{g3}} \tag{3}$$

where all the symbols have the same meaning as in Eq. (1). The outcome is shown in Fig. 4 (T_{gF} versus experimental T_g). The miscible sPMMA ternary T_g values are represented by solid triangle symbols. The empty circles denote the iPMMA ternary T_g results. The dashed line represents when experimental T_g values are equal to T_{gF}. It is obvious that all the experimental T_g data are larger than Fox predictions except for the two low T_g values. Two iPMMA ternaries with 25% PVPh have T_g values lower than Fox prediction likely due to low degree of hydrogen bonding. When the experimental T_g values are lower than 100 °C, the Fox predictions are more or less satisfactory because of probably insignificant hydrogen bonding. The larger experimental ternary T_g values (especially those larger than 100 °C) observed than T_{gF} are because of high degree of hydrogen bonding. For T_g values higher than 100 °C, most iPMMA ternary exhibits larger T_g values than sPMMA ternary likely because of stronger inter-hydrogen bonding among the blends.

Attempts were made to predict the miscible ternary T_g values. The approach is likely new to the best of our knowledge and described as follows. A miscible ternary consisting of a pseudo-binary mixture of PMMA/PVPh and PVAc/PVPh entities is assumed. Therefore the contribution from PMMA/PVAc is neglected since PVPh is acting as a compatibilizer between PMMA and PVAc. The Kwei equation is modified and proposed as below for the ternary:

$$T_g = w_1 T_{g1} + w_2 T_{g2} + w_3 T_{g3} + q_{12} w_1' w_2 + q_{13} w_1'' w_3 \tag{4}$$

where T_g is the glass transition temperature of a blend, T_{gi} and w_i are the glass transition temperature and the weight fraction of polymers i, respectively ($i = 1, 2, 3$). w'_1 and $w''_1(w'_1 + w''_1 = 1)$ represent the fraction of PVPh distributed between PVPh/PMMA and PVPh/PVAc entities. q_{12} and q_{13} represent the binary interaction parameter between different corresponding components. Components 1–3 denote PVPh, PMMA and PVAc, respectively. The q_{12} values obtained previously in binary blends are 66.8 and 86.2 for PVPh/sPMMA and PVPh/iPMMA, respectively. The concentration power equation for describing the composition dependence of the T_g of the compatible binary blend was developed by Brekner, Schnieder and Cantow [16]. Since the T_g of PVAc/PVPh blends showed both negative and positive deviation from weight average, a composition dependence of q_{13} (similar to Brekner's approach) was adopted. First, q_{13} values of three compositions were calculated similar to PMMA/PVPh blends by Eq. (2) (the simplified Kwei equation). Then a linear regression of q_{13} as a function of PVPh weight fraction was performed. The following equation was obtained:

$$q_{13} = \frac{-96.3 + 245.4w''_1}{w''_1 + w_3} \tag{5}$$

where w'_1/w''_1 is likely a function of w_2, w_3, q_{12} and q_{13}. The tentative simplification is to set w'_1/w''_1 equal to w_2/w_3 since the PMMA/PVPh interaction and the PVAc/PVPh interaction are almost the same. The T_{gk} values (modified Kwei predictions) estimated through Eqs. (4) and (5) are tabulated in Table 5 along with estimated w'_1, w''_1 and q_{13} values. The results were plotted versus experimental T_g and shown in Fig. 5. The dashed line represents when experimental T_g values are equal to T_{gk}. The agreement between modified Kwei predicted T_g values and experimental results are almost quantitatively good and improved a lot than previous Fox predictions. Improvements are corroborated by computing the average differences between predictions and data. The difference between T_{gk} and experimental T_g points (in Fig. 5) was calculated to be 6.0 ± 4.2 °C. However, much larger value (11.5 ± 6.9 °C) was estimated between Fox predictions and T_g data in Fig. 4. The three high T_g points in Fig. 5 are still not well fitted by the proposed equation but a little closer to the prediction. The blends with three highest T_g points all have 75% PVPh. Maybe the ternary interaction (PMMA–PVPh–PVAc) is significant at high PVPh composition thus causing the glass transition temperatures much higher than prediction. Finally, future work to validate this modified Kwei equation with data obtained from other ternary blends involving hydrogen bonding is currently pursued in this laboratory.

Table 5
Glass transition temperatures estimated by a modified Kwei equation

	w'_1 (%)	w''_1 (%)	q_{13}	T_{gk} (°C)	T_g (°C)
PVPh/sPMMA/PVAc					
1. (50.0/12.5/37.5)	12.5	37.5	26.30	94.8	93.3
2. (75.0/6.3/18.7)	18.9	56.1	87.75	113.2	105.8
3. (49.9/25.0/25.1)	24.9	25.0	26.15	104.8	102.2
4. (74.9/12.6/12.5)	37.6	37.3	87.75	114.9	114.1
5. (49.9/37.6/12.5)	37.45	12.45	26.15	117.9	118.8
6. (75.0/18.7/6.3)	56.1	18.9	87.75	120.2	133.7
PVPh/iPMMA/PVAc					
1. (25.0/18.8/56.2)	6.27	18.73	−34.95	66.0	60.2
2. (50.0/12.5/37.5)	12.5	37.5	26.30	89.6	90.5
3. (75.0/6.3/18.7)	18.9	56.1	87.75	110.7	99.6
4. (25.0/37.5/37.5)	12.5	12.5	−34.95	76.2	66.2
5. (49.8/25.1/25.1)	24.9	24.9	25.91	94.8	102.9
6. (75.0/12.5/12.5)	37.5	37.5	87.75	110.3	123.5
7. (25.0/56.2/18.8)	18.7	6.3	−34.95	87.5	81.6
8. (50.1/37.4/12.5)	37.55	12.55	26.30	103.9	107.0
9. (75.0/18.7/6.3)	56.4	18.7	87.75	114.4	129.9

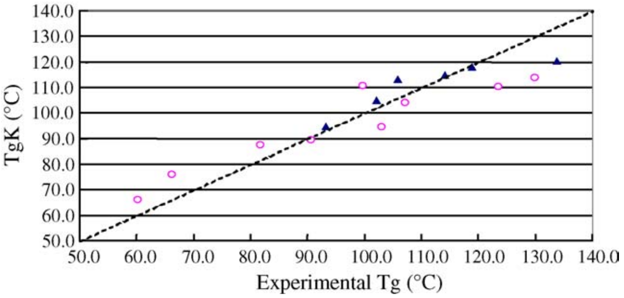

Fig. 5. Modified Kwei predicted T_g vs. experimental T_g: (▲) sPMMA; (○) iPMMA.

4. Conclusion

PMMA and PVAc are almost completely immiscible regardless of tacticity. PVPh is miscible with both iPMMA and PVAc because of inter-hydrogen bonding in accordance with literature. Miscibility was also found between sPMMA and PVPh in this report slightly different from previous finding. The low molecular weight of PVPh induces better miscibility. A ternary blend consisting of iPMMA, PVAc and PVPh was found to be completely miscible. However, the same ternary blend using sPMMA instead of iPMMA demonstrated immiscibility at ca. 25% PVPh. The major difference is as follows. The solubility of PVAc in iPMMA is slightly better than that of PVAc in sPMMA. Therefore the $\Delta\chi$ effect is weaker in PVAc/iPMMA than in PVAc/sPMMA blends. The inter-hydrogen bonding between iPMMA and PVPh is closer in strength to PVAc/PVPh interaction than sPMMA/PVPh interaction. The iPMMA ternaries probably exhibited weaker ΔK effect than sPMMA ternaries. Miscibility encountered in iPMMA ternaries is probably driven by both weak $\Delta\chi$ and small ΔK effects in concert. The miscible T_g values of the ternaries were described by the Fox equation qualitatively. However, the T_g values estimated by a proposed modified Kwei equation demonstrated much better agreement with experimental T_g. A miscible ternary consisting of a pseudo-binary PMMA/PVPh and PVAc/PVPh entities was assumed. Two incorporated binary interaction parameters enable the Kwei equation to successfully predict the glass transition temperatures of miscible ternaries.

Acknowledgments

The financial support by the National Science Council of Taiwan, R.O.C. NSC 91-2216-E-041-005 is highly appreciated. The insightful discussion with Prof. T.K. Kwei is greatly acknowledged.

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